

NTICPO107A

PROCESS FOR INFUSING AN ALKALI METAL
NITRITE INTO A SYNTHETIC RESINOUS MATERIAL

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Cross-reference to related application: This application is a continuation-in-part application of Ser. No. 10/347,661 filed 20 January 2003.

FIELD OF THE INVENTION

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The present invention relates to a process for transferring a particular class of salts, namely an alkali metal salt, from supercritical carbon dioxide in which the salt is in solution, directly into a synthetic resinous substrate, for example, a film or shaped article, in which the only other way of incorporating the salt is by physically mixing it into the polymer, then melt-processing the mixture.

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The Problem:

It is desirable to impregnate polymeric film or a shaped polymeric article with a combination of an inorganic salt and a phenol, namely an alkali metal nitrite and a hindered phenol, which article may have been molded under temperature conditions deleterious to the combination; and, to ensure that the nitrite and phenol are uniformly distributed throughout the body of the article. The problem is particularly serious when an article is molded from a substantially transparent, water-white polyolefin protected with a hindered phenol which is degraded when the polyolefin is molded at a temperature above about 121°C (250°F), as evidenced by the polymer turning yellow. It is also desirable that crystalline particles of the ingredients infused into the polymer, be invisible to the human eye. Such invisibility results when the particles are smaller than about 10 μm (micrometers) equivalent diameter. By "equivalent diameter" is meant the diameter of a spherical particle of equal volume. All references herein to particle size refer to the equivalent diameter. At present, the sodium nitrite is incorporated into the polymer as particles in the size range from about 10 μm to 44 μm , all of which pass through a 325 mesh screen or 45 μm (Standard Test Sieves), as smaller particles do not

get uniformly distributed when an article is molded, or film is extruded, with polymer containing the smaller particles. Further, non-uniformly distributed particles, whether large or small in the range from about 10 – 44 μm , causes the polymer's melt-processed surface to be noticeably rough to the touch, compared to a smooth surface of film of the same polymer without any sodium nitrite particles. In film, or molded articles with a cross-section of less than 50 μm (0.002" or 2 mil), particles smaller than 10 μm are not visible to the human eye; larger particles are. The limitation of concentration is necessary because a concentration of particles in an amount of 2% by weight, or more, in the polymer substrate becomes visible to the human eye, even if the particles are smaller than 10 μm . Though the emphasis is on the temperature sensitivity of a protective antioxidant or uv light stabilizer, a biodegradable polymer may itself be equally sensitive.

BACKGROUND OF THE INVENTION

The conventional way of introducing a solid ingredient into a polymer is by melt- processing a mixture of the ingredient and polymer, either in an extruder, or by plasticizing the polymer sufficiently so as to be able to mix the ingredient into the plasticized mass. Such a procedure may be applicable if an ingredient can withstand a temperature at which the polymer is plasticizable, in the case of polyvinyl chloride (PVC), this temperature is in the range from about 180°C to about 200°C.

When the properties of an ingredient are to be preserved when it is incorporated into a polymer, melt-processing an ingredient which is degradable at a temperature required for melt-processing is thus negated.

In the prior art, supercritical carbon dioxide has been used mainly to extract an organic ingredient from a substrate in which it is distributed, or to separate one organic compound from another. Each of the foregoing relies upon the known higher solvent power of a fluid as its density increases. A supercritical fluid is sufficiently dense to swell a polymer even if the polymer is essentially insoluble in the supercritical fluid, by virtue of forcing molecules of the supercritical fluid into the pores of the polymer, as taught by U.S. Patent No. 5,340,614 to Perman et al., provided a carrier liquid was also

used to “carry” the additive into the pores of the polymeric substrate. However, Perman et al were unconcerned with either uniformity of distribution of infused particles, or their size, and make no mention of either.

Unlike the foregoing, U.S. Patent No. 4,820,752 teaches “infusing into a rubber
5 or plastic polymeric material” (*sic*) any additive, liquid or solid, which has a “degree of solubility in said polymeric material when said polymeric material is in a swollen state”, using a normally gaseous fluid which could be compressed to supercritical conditions. Clearly, solubility of the additive in the polymer is required, the degree of solubility being at least 0.1 percent, and under the high pressure conditions described,
10 any microporous polymer substrate will necessarily become swollen.

Moreover, it is not clear whether the fluid is required to dissolve either the additive or the polymer, or both, or simply swell the polymer, such equivocation being stated as follows: “A fluid may have sufficient solvent or swelling power to be useful in practicing this invention if sufficiently compressed at temperatures above, equal to, or
15 below the critical temperature of the fluid” (see ‘752 patent, col 4, lines 45-49). Evidently the only requirement of the fluid to provide all the necessary properties to infuse a polymer with any additive is that the fluid be derived by compressing a normally gaseous fluid. Such evidence is provided in Examples 1 and 2 teaching the use of carbon dioxide at 22°C and pressure of 59.6×10^5 Pa (or 5960 kPa), and in Examples
20 3 and 4 at 22°C and pressure of 65.1×10^5 Pa (or 6510 kPa), under which conditions carbon dioxide is not supercritical. The supercritical conditions for carbon dioxide are 31.4°C and 73.4 atm (7435.42 kPa). Only Example 6 deals with supercritical carbon dioxide which was used to impregnate a polyurethane sheet with progesterone, the solubility of which, in supercritical carbon dioxide, or lack thereof, was not stated.

25 Still further, the ‘752 patent states: “In accordance with the present invention, an additive desired to be included in a rubber or plastic composition is dissolved in a compressed normally gaseous fluid.” (‘752, col 2, lines 16-17) but requires only that the additive have a “degree of solubility” stated as follows: “The fluid and additive are chosen so that the additive has a degree of solubility in the polymer into which it is to
30 be infused and so that the solution of fluid and additive has a degree of solubility in the polymer and is capable of swelling the polymer.” (‘752, col 2, lines 29-33). If the

“degree of solubility” included essentially complete solubility, then the polymer too would be dissolved in the “the solution of fluid and additive”.

As evidenced by illustrative example 1, “other sample chips were exposed in a pressure vessel to carbon dioxide in the presence of solid naphthalene at room
5 temperature and a pressure of 59.6×10^5 pascals for 92 hours;” indicating that all the naphthalene was not in solution. Thus This may be attributable to the fact that the carbon dioxide was not under cupercritical conditions. The only example where supercritical carbon dioxide was used (Example 6) states that a sheet of polyurethane
10 “was exposed to progesterone in the presence of carbon dioxide at a temperature of 45°C and a pressure of 151.6×10^5 pascals for 4.5 hr” indicating not all the progesterone was in solution. Thus, Berens et al were unaware that solid particles of relatively large size could be transported if fully dissolved in supercritical carbon dioxide to form a solids-free solution, and the solids redeposited in a polymer substrate as micronized crystals.

15 Persons of ordinary skill in the art are well aware that the solubility of an additive in a supercritical fluid, and in supercritical carbon dioxide in particular, cannot be predicted. This is particularly true for inorganic salts. For example, as shown below, sodium nitrite is soluble in supercritical carbon dioxide, but sodium chloride is not. In view of such unpredicatbility it should now be evident that a teaching that any normally
20 solid additive, whether organic or inorganic, may be transferred from a liquid under pressure into a swellable polymer, as taught in the ‘752 patent, is at best overly broad.

U.S. Patent No. 4,290,912 issued to Boerwinkle et al, about two decades ago, disclosed that an inorganic nitrite, and in particular, an alkali metal nitrite, e.g. potassium nitrite, sodium nitrite and calcium nitrite, in combination with a 2,4,6-
25 trisubstituted phenol provided an effective volatile corrosion inhibitor (VCI) when distributed in a lower ($\text{C}_2 - \text{C}_5$) polyolefin (PO) polymer. A specific ‘912 combination comprised about equal parts (1.485 phr each) by weight of sodium nitrite and a 2,4,6-tri-substituted phenol containing 9 to 24 carbon atoms, specifically 2,6-di-tert-butyl-4-methyl phenol, along with small amounts of one or more inert ingredients such as
30 fumed silica and oleyl alcohol which are known to possess no anti-corrosive properties. Effectiveness of the ‘912 film was unconcerned with the primary particle size of the

sodium nitrite because the '912 patent did not address the problems (i) of uniformity of distribution, (ii) of particle size, or (iii) of maintaining transparency of extruded film or molded articles having smooth surfaces.

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SUMMARY OF THE INVENTION

It has been discovered that an alkali metal nitrite which is substantially insoluble in liquid carbon dioxide which is not under supercritical conditions, becomes highly soluble when the conditions become supercritical. The expectation that all alkali metal salts are highly soluble in supercritical carbon dioxide is negated by the substantial insolubility of sodium chloride in supercritical carbon dioxide. Moreover, one may dissolve crystals of an alkali metal nitrite larger than 10 μm in supercritical carbon dioxide and by impregnating a polymer substrate with the solution, deposit crystals smaller than 10 μm in the substrate. The most preferred alkali metal nitrite is sodium nitrite.

A process for rapidly infusing a synthetic resinous substrate with an alkali metal nitrite, comprises (a) essentially completely dissolving the alkali metal nitrite in supercritical carbon dioxide to form a solids-free solution having from about 1 to 15% by weight of the alkali metal nitrite; (b) contacting the synthetic resinous substrate with the solution for a time sufficient to transfer at least a portion of the alkali metal nitrite into the synthetic resinous substrate while maintaining the carbon dioxide under supercritical conditions; and, (c) decreasing pressure or temperature, or both, on the synthetic resinous material sufficiently to evolve carbon dioxide and leave micronized solid alkali metal nitrite crystals in an amount less than 2% by weight essentially uniformly distributed in the synthetic resinous substrate. If desired, up to about 15% by weight of sodium nitrite or potassium nitrite may be transported and deposited in the substrate if transparency of the substrate is irrelevant, because the substrate tends to become opaque.

By "micronized" crystals is meant that the major portion by weight of the crystals have an average particle size smaller than 10 μm . By "rapidly" is meant that from about 0.1 to less than 2% of the alkali metal nitrite crystals go into solution in the supercritical carbon dioxide in less than 30 minutes. Such speed is essential for the

impregnation stage of a commercially viable two-stage process in which it is necessary to recycle and recompress to supercritical conditions the recovered carbon dioxide.

By "uniformly distributed" is meant that the uniformity of dispersed particles in the film may be quantified by known microscopic techniques, or by a blown film test.

- 5 In the blown film test, the polymer containing solid powder particles is extruded through a blown film apparatus which produces a film about 0.025 mm (1 mil) thick, and this film is placed over a light source of appropriate wavelength and intensity to enable one to quantify the number of particles which show up as "imperfections"; and the size of each is also visible under appropriate magnification. No unit area of the film
10 appears to have a substantially higher concentration of particles than another.

- The foregoing process is preferably carried out with the alkali metal nitrite in combination with an organic compound which forms a solids-free solution in supercritical carbon dioxide, in a two-stage process comprising, (i) dissolving an alkali metal nitrite and the organic compound in carbon dioxide held in an autoclave under
15 supercritical conditions to form a solution containing from about 1 to 15% by weight of sodium nitrite and organic compound, (ii) filtering the solution to ensure that substantially no particulate solids are present in filtered solution; (iii) contacting a polymeric substrate with the filtered solution for less than 30 minutes so as to transfer enough sodium nitrite and organic compound into the substrate so as to infuse it with
20 less than 2% by weight of an alkali metal nitrite and organic compound. The impregnated substrate necessarily becomes swollen due to the high-pressure entry of supercritical carbon dioxide molecules, but such swollen condition reverts to normal when the carbon dioxide leaves the substrate.

- In another embodiment of the process, the supercritical carbon dioxide may be
25 combined with a second fluid miscible (forming a common supercritical phase) with carbon dioxide under supercritical conditions, which second supercritical fluid, present in a minor amount by weight relative to the carbon dioxide, facilitates dissolution of an organic compound such as a hindered phenol or aromatic amine, in the common supercritical phase. A preferred second fluid is selected from the group consisting of
30 ethylene, ethane, nitrous oxide, chlorotrifluoromethane and trifluoromethane which have critical temperatures and pressures in the vicinity of those for supercritical carbon

dioxide and can be readily recovered and recycled together.

The process described herein may be repeated on a polymer substrate which has been previously impregnated, and from which the impregnated solid crystals have been removed, as for example, by evolution over a long period of time, as when sodium
5 nitrite crystals are used as a VCI.

DETAILED DESCRIPTION OF THE INVENTION

A fluid, either gas or liquid at room temperature (25°C) and pressure (1 atm or 14.7 psia or 101.3 kPa), when subjected to the necessary combination of pressure and
10 temperature, both of which are higher than the critical pressure and critical temperature of the fluid, produces a supercritical fluid. Above its critical temperature (T_c), a gaseous fluid cannot be converted to a liquid regardless of the pressure exerted on the gas.

It is essential that alkali metal nitrite crystals be essentially completely soluble
15 in supercritical carbon dioxide. When a dispersion of such crystals, smaller than 45 μm , in supercritical carbon dioxide, is contacted with a polyolefin article, before the crystals are dissolved, the crystals become non-uniformly embedded in the surface of the polymer, and are readily visible to the human eye.

Example 1

20 A dispersion of sodium chloride crystals smaller than 45 μm (more than 90% are in the range from 10 – 44 μm) is essentially insoluble in supercritical carbon dioxide, as evidenced by the following experiment:

100 g of the sodium chloride crystals are deposited in a 300 ml Micro Series pressure vessel, referred to as the “main” pressure vessel, equipped with a propeller
25 stirrer and with a transparent glass window through which the deposited crystals are visible. The main pressure vessel is closed and charged with carbon dioxide gas from a cylinder using a compressor which pressurizes the vessel to 102.04 atm or 10.35 Mpa (1500 psi) and the temperature of the vessel is maintained at 35°C so that supercritical conditions are obtained. The outlet from the vessel is led through a fresh and
30 uncontaminated 1 μm filter to a depressurizing valve through which the contents of the

vessel are withdrawn into a second pressure vessel from which the carbon dioxide is to be recovered.

The stirrer is started and is kept running for 10 minutes at 700 rpm. Upon stopping the stirrer, the crystals are still visible. When the vessel is depressured through the filter, the filter is removed and flushed with distilled water which is tested for the presence of NaCl by the addition of a 1 molar solution of silver nitrate. A very slight white haze develops indicating very little sodium chloride is present.

The sodium chloride crystals are removed from the vessel and weighed – their weight is essentially unchanged indicating very little of the salt went into solution.

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Example 2

A dispersion of the sodium nitrite crystals smaller than 45 μm is essentially insoluble in liquid carbon dioxide, not under supercritical conditions, as evidenced by the following experiment:

In a manner analogous to that described in Example 1 above, 100 g of the sodium nitrite crystals are deposited in the same main pressure vessel fitted with a freshly cleaned 5 μm filter. The vessel is then pressurized with carbon dioxide to 54.4 atm or 30 Mpa (800 psi) and the temperature of the vessel is maintained at 25°C so that liquid is visible in the vessel. The stirrer is run for 10 min at 700 rpm and then stopped. The vessel is then depressurized through the 1 μm filter. The filtrate is collected in the second pressure vessel which is gradually depressurized so as to recover the carbon dioxide. Examination of the interior of the second pressure vessel shows that there are no crystals left. As before, after the main pressure vessel is depressurized, the filter is removed and washed with distilled water and the water analyzed for sodium nitrite which is soluble in an amount of 81.5 g/ 100 ml of water at 15°C. Less than 150 ppm of sodium nitrite is found, indicating that the sodium nitrite crystals are essentially insoluble in liquid, but not supercritical carbon dioxide.

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Example 3

Sodium nitrite crystals smaller than 45 μm are essentially completely soluble in carbon dioxide under supercritical conditions, as evidenced by the following experiment:

In a manner analogous to that described in Example 1 above, 100 g of the sodium nitrite crystals are deposited in the same main pressure vessel fitted with a freshly cleaned 5 μm filter. The vessel is then pressurized with carbon dioxide to 102.04 atm or 10.35 Mpa (1500 psi) and the temperature of the vessel is maintained at 35°C so that supercritical conditions are obtained. The stirrer is run for 10 min at 700 rpm and then stopped.

No crystals are visible in the window of the vessel. When the vessel is depressurized and removed to be inspected, no crystals are recovered.

As before, the second pressure vessel is gradually depressurized through the 1 μm filter until all the carbon dioxide is recovered. Examination of the interior of the vessel shows deposited crystals which are recovered and weighed. Additionally, after the main vessel is depressurized, the filter is removed and washed with distilled water five times. All the wash water is collected and concentrated to precipitate the sodium nitrite crystals which are weighed. The combined weight of the crystals recovered from the second pressure vessel and the very small amount recovered from the filter, is more than 99 gm, indicating that essentially all the crystals went into solution in the supercritical carbon dioxide.

The supercritical properties of a variety of compounds are shown below in Table 1.

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Table 1

Fluid	Critical Temperature (°C)	Critical Pressure (MPa)
Carbon Dioxide	31.4	7.38
Nitrous Oxide	36.5	7.26
Ethylene	9.3	5.03

Fluid	Critical Temperature (°C)	Critical Pressure (MPa)
Ethane	32.3	4.88
Trifluoromethane	25.2	4.83
Chlorotrifluoromethane	29.9	3.92
Ethanol	240.8	62.2
Acetone	234.9	46.4

As is evident from the data in the above Table, ethanol and acetone would require conditions very different from those required to make supercritical carbon dioxide.

- 5 Polymers which lend themselves to be impregnated or may be formed from any rubber or polymer capable of being swollen by at least about 2 percent by volume, or by at least about 5 percent by volume, or even by at least about 7 percent by volume by the supercritical fluid being utilized in the present invention. Such polymers include natural rubbers, polyisoprene polymers, styrene-butadiene polymers, butyl rubbers,
- 10 chloroprene polymers, polyamides, polyimides, polyesters, nitrile rubbers, polyacrylic polymers, polystyrene polymers, fluoro polymers (e.g., polytetrafluoro ethylene or polyvinylidene fluoride), vinyl chloride polymers, vinylidene chloride polymers, polycarbonate polymers, polyurethane polymers, polyacetylenes and polyolefins. In another embodiment, the present invention can also be utilized to infuse one or more
- 15 additives into a precursor or resin used to form the above-listed polymer compositions. Most preferred are polyolefins, and polyethylene (PE) and polypropylene (PP) in particular which may be required to be substantially transparent.

The process described herein also enables one to infuse one or more alkali metal nitrites and organic compounds into a biodegradable polymer, biodegradable polymer precursor or resin or a pre-formed biodegradable polymer article. Any polymer which exhibits biodegradability can be utilized in conjunction with the present invention.

5 Examples of suitable biodegradable polymers include, but are not limited to, biodegradable polyesters (e.g., linear poly ϵ -caprolactone (PCL)), biodegradable polylactic acid polymers, biodegradable polyester amide polymers, biodegradable polyester urethane polymers and biodegradable copolymers of any combination of two or more of the above.

10 Though any organic compound soluble in supercritical carbon dioxide may be combined with the less than 2% by weight of alkali metal nitrite in solution, most preferred are VCIs such as are disclosed in U.S. Patent Nos. 4,290,912; 5,320,778 and 5,855,975, which are incorporated by reference thereto as if fully set forth herein; and, commonly used antioxidants such as the 2,4,6-tri-substituted phenols exemplified by
15 BHT (2,4,6-tributyl hydroxy toluene)

To illustrate that a PE substrate may have even larger amounts of sodium nitrite crystals than 2% by weight, deposited in the polymer, the following experiments are set forth:

Two rectangular pieces of PE film, 4.5" x 2.5" x 0.0039", and a piece of
20 polyethylene tubing having an outside diameter of 1.75" and 0.0039" thick, are weighed and placed in the main pressure vessel described above. The vessel is then charged with a 20 wt % solution of NaNO_2 in supercritical CO_2 at a temperature of 50°C and a pressure of 176.9 atm (2600 psi) for about 30 minutes.

After 30 minutes, the items are removed and reweighed. The two rectangular
25 films of PE show a weight gain which correlates to an infusion rate of 9.38 wt % and 10.87 wt %. The PE tubing shows a weight gain which correlates to an infusion rate of 6.64 wt %.

As can be seen from Tables 2 to 4 below, as the time, temperature or pressure at which the infusion or diffusion process is conducted varies, so does the amount of
30 additive incorporated into the polymer. For the results listed in Tables 2 to 4, PE pellets having a diameter of about 0.2" are used with NaNO_2 in solution in CO_2 under the

conditions described immediately above.

Table 2

Pressure (atm/psi)	Weight Percent Increase
163.3 atm (2400 psi)	3.06
204.1 atm (3000 psi)	8.50

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Table 3

Time (hr)	Weight Percent Increase
0.5	3.06
1.0	8.50
3.0	14.84

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Table 4

Temperature (°C)	Weight Percent Increase
40	5.26
50	3.06
60	4.46

From the foregoing it is evident that the amount of alkali metal nitrite crystals
5 which can be deposited in a polymer substrate may be controlled by controlling the time
of immersion and the particular conditions of the supercritical phase.